

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 052 297 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.11.2000 Bulletin 2000/46

(51) Int. Cl.⁷: C22C 1/05, C22C 29/04

(21) Application number: 00109356.6

(22) Date of filing: 02.05.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

- Zwinkels, Marco
169 35 Solna (SE)
- Piirhonen, Anders
128 34 Skarpnäck (SE)
- Rolander, Ulf
112 64 Stockholm (SE)

(30) Priority: 03.05.1999 SE 9901581

(71) Applicant: SANDVIK AKTIEBOLAG
811 81 Sandviken (SE)

(74) Representative:
Taquist, Lennart et al
Sandvik AB
Patent Department
811 81 SANDVIKEN (SE)

(72) Inventors:
• Weini, Gerold
125 52 Älvsjö (SE)

(54) Method for producing Ti(C,N)-(Ti,Ta,W)(C,N)-Co alloys for cutting tool applications

(57) The present invention relates to a method for manufacturing a sintered body of carbonitride alloy with titanium as the main component and at least 2 at% of each of tantalum and tungsten and that the atomic N/(C+N) ratio is 25-50 at% and cobalt as the binder phase and which does not have any compositional gradients or center porosity concentration after sintering. This is achieved by processing the material in a specific sintering cycle with particular nitrogen and carbon monoxide partial pressures to obtain a lower melting point of the liquid phase in the interior of the body than in the surface while balancing the gas atmosphere outside the body with the alloy composition during all stage of the liquid phase sintering.

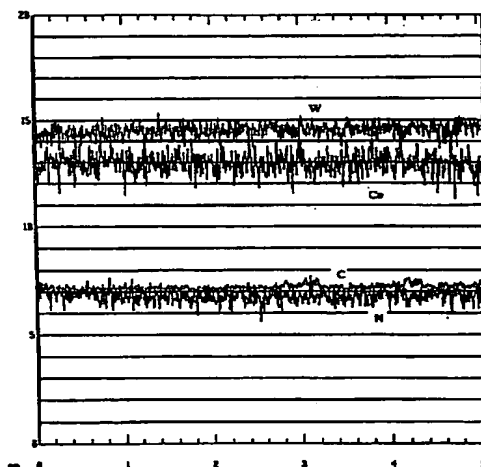


Fig. 1

EP 1 052 297 A1

Description

[0001] The present invention relates to a method for manufacturing a sintered body of carbonitride alloy with titanium (Ti) as the main component and cobalt (Co) as the binder phase and which does not have any compositional gradients or center porosity concentration after sintering. This is achieved by processing the material in a specific manner to obtain a lower melting point of the liquid phase in the interior of the body compared to the surface while balancing the gas atmosphere outside the body with the alloy composition during all stages of the liquid phase sintering.

[0002] Titanium-based carbonitride alloys, so called cermets, are today well established as insert material in the metal cutting industry and are especially used for finishing. They comprise carbonitride hard constituents embedded in a metallic binder phase. The hard constituent grains generally have a complex structure with a core surrounded by a rim of a different composition. In addition to titanium, group VIa elements, normally both molybdenum and tungsten and sometimes chromium, are added to facilitate wetting between binder and hard constituents and to strengthen the binder by means of solution hardening. Group IVa and/or Va elements, i.e., zirconium, hafnium, vanadium, niobium and tantalum, are also added in all commercial alloys available today. All these additional elements are usually added as carbides, nitrides and/or carbonitrides. The grain size of the hard constituents is usually $<2\text{ }\mu\text{m}$. The binder phase is normally a solid solution of mainly both cobalt and nickel. The amount of binder phase is generally 3-25 wt%. Other elements are sometimes added as well, e.g. aluminium, which are said to harden the binder phase and/or improve the wetting between hard constituents and binder phase. Of course, commercially available raw material powders also contain inevitable impurities.

[0003] The most important impurity is oxygen, due to its high affinity to titanium. A normal impurity level for oxygen has historically been $<0.3\text{ wt}\%$. Recently, due to improved production methods for titanium-based raw materials, this level has been decreased to $<0.2\text{ wt}\%$, especially for grades with low nitrogen content. Very high oxygen levels are generally avoided since this may cause formation of carbon monoxide (CO) after pore closure during liquid phase sintering, which in turn leads to excessive porosity.

[0004] Common for all cermet inserts is that they are produced by the powder metallurgical methods of milling powders of the hard constituents and binder phase, pressing to form green bodies of desired shape and finally, liquid phase sintering the green bodies. Provided that good wetting is obtained between the liquid and the solid hard phase grains, strong capillary forces are obtained. The action of these forces is to shrink the porous body essentially isotropically, thereby eliminating porosity. The linear shrinkage is typically 15-30 %.

[0005] Sintering of titanium carbonitride-based cermets is a complex process, which requires precise control of all steps to obtain a sintered body with desired properties. Generally, after dewaxing, the material is heated under vacuum or in an inert atmosphere to 1250-1350 °C to enable desoxidation and denitrification of the material. Further heating to the final sintering temperature and subsequent cooling is normally done under vacuum or in an atmosphere that may contain both inert and reactive gases. Each of the steps influences the properties of the sintered material and must therefore be optimized carefully.

[0006] Conventional sintering processes yield sintered material with several drawbacks, such as lack of toughness and wear resistance. The sintered bodies commonly have a concentration of pores in the center and a surface with varying degrees of enrichment or depletion of the binder phase. Various attempts have been made to improve process control by varying the gas atmosphere during sintering.

[0007] Sintering in nitrogen (N_2), accomplished in various ways, provides a means to limit denitrification, which is especially useful for cermets with high nitrogen content.

[0008] US 4,990,410 discloses a process for producing a cermet by liquid phase sintering in 0.1-20 torr N_2 at temperatures $\geq 1300\text{ }^\circ\text{C}$. A nitrogen atmosphere is proven useful for modification of the near surface properties of sintered cermet bodies. US 5,059,491 discloses a process for producing a cermet with maximum hardness at a depth between 5 and 50 μm from the surface by liquid phase sintering in N_2 and cooling in vacuum. US 4,985,070 discloses a process for producing a high-strength cermet, which is accomplished by sintering the material in progressively increasing nitrogen pressure. US 5,145,505 discloses a process for producing a tough cermet with a binder-depleted surface by sintering in 5-30 torr N_2 .

[0009] Sintering in CO has been found useful for obtaining improved control over the surface of sintered cermet bodies. WO 99/02746 discloses a process for producing sintered bodies without the common binder phase layer of 1-2 μm thickness on the surface by sintering in CO at pressures of 1-80 mbar.

[0010] Sintering in CO-N_2 mixtures has been attempted to obtain improved properties of sintered bodies. US 5,856,032 discloses a process for producing Ti(C,N)-based cermets by liquid phase sintering in CO-N_2 mixtures. The gas mixture is used to modify the surface-near zone of the sintered body, down to a depth of 600 μm . The desired composition of the gas mixture is dependent on the nitrogen content of the hard constituents whereas the total pressure needed is determined by the binder content. The sintered bodies are characterized in that the content of the Co and/or Ni-binder in a surface layer of 0.01-3 μm depth in relation to the underlying core amounts to $\leq 90\text{ }\%$ by mass in all cases.

[0011] US 6,017,488 discloses a process for producing sintered cermet bodies with Co binder. Sintering is per-

formed in CO-N₂ mixtures, in which the partial pressures are kept below 20 mbar. The sintered bodies have a unique feature in that they have a macroscopic Co gradient, in which the Co content decreases essentially monotonously from the center of the body to its surface and reaches a Co content at a depth of 0-10 µm from the surface of 50-99 % of that in the center.

[0012] A series of titanium carbonitride-based alloys with Co binder are disclosed in Swedish patent applications 9901582-88, 9901583-6 and 9901584-4 corresponding to European Patent Applications Nos. , and filed concurrently herewith. These have superior performance in metal cutting applications, both with and without single or multiple layer wear-resistant coatings of carbides or nitrides of Ti and/or aluminum oxide. They show a unique behavior during sintering, being quite different from conventional cermets with Ni-Co binder. One feature is the high content of Ta, i.e. ≥2 at%, preferably 4-7 at%, which increases the nitrogen activity in the material during sintering. Another feature is the optimization of the raw materials that has led to significant improvement of performance in metal cutting. Due to these two features these materials differ substantially from the conventional and hence they require a sintering process, unlike the ones that are commonly used. If they are sintered according to the processes disclosed in US 6,017,488 or US 5,856,032, they will melt in the conventional way, i.e. from the surface inwards, leading to gas entrapment and unacceptable porosity, which must be avoided in order to fully utilize the potential of these materials.

[0013] It is an object of the present invention to provide a method of manufacturing said class of titanium carbonitride-based alloys having Co as a binder and high Ta content.

[0014] In one aspect of the invention, the hard phase of the alloy for which the invented process is useful, has an N/(C+N) ratio of 25-50 at%. The Ta content is at least 2 at%, preferably 4-7 at%. The W content is at least 2 at%, preferably 3-8 at%. The Co content is 5-25 at%. A sintered body, manufactured according to the invented process, is essentially free of compositional gradients throughout the body. Moreover, such a body contains porosity in the class A06 or less, preferably A04 or less, evenly distributed throughout the volume, i.e. without a concentration of pores in the center of the body. The somewhat higher porosity is due to the high Ta content, leading to a very high nitrogen activity in the alloy.

[0015] In another aspect of the invention, there is provided a method of manufacturing a sintered carbonitride alloy in which powders of carbides, carbonitrides and/or nitrides are mixed with Co to a prescribed composition and pressed into green bodies of desired shape. The green bodies are liquid phase sintered in a controlled gas atmosphere at a temperature 1370 - 1550 °C.

Fig. 1 is an EMPA (Electron Micro Probe Analysis) line scan across an insert of a Ti(C,N)-(Ti,Ta,W) (C,N)-Co alloy sintered in the presently invented process.

Fig. 2 is an EMPA line scan across an insert of a Ti(C,N)-(Ti,Ta,W)(C,N)-Co alloy sintered in a reference process.

Fig. 3 is an EMPA line scan across an insert of a Ti(C,N)-(Ti,Ta,W)(C,N)-Co alloy sintered in a reference process.

Fig. 4 is an EMPA line scan across an insert of a Ti(C,N)-(Ti,W)(C,N)-Co alloy sintered in a reference process.

[0016] It has quite surprisingly turned out, for the alloy class specified above, that by utilizing the invented process a sintered body without a macroscopic Co gradient can be obtained while maintaining the favorable melting, i.e. nucleation in the center propagating towards the surface. This favorable outcome is achieved by dewaxing the green bodies, followed by increasing the temperature under vacuum to 1250-1350 °C to allow desoxidation and controlled denitrification of the hard phase grains. The denitrification is controlled by the temperature increment and temperature plateaus at suitable levels. Subsequently, sintering is carried out in a predefined gas atmosphere. Different gas compositions are required for

- (1) the temperature rise up to the final sintering temperature,
- (2) the plateau at the final temperature and
- (3) the temperature decrease to ≤1200 °C.

(1) The partial pressures of CO and N₂ should be kept constant or increased stepwise or monotonously while increasing the temperature up to the final sintering temperature to balance the increasing gas generation rate in the green bodies. Too low pressures will result in macroscopic Co gradients, whereas too high pressures will revert the melting process, leading to center porosity concentration. The levels for CO and N₂ for the onset of sintering are 0.25-3 mbar, preferably 0.5-1.5 mbar. The partial pressure levels for CO and N₂ when reaching the final sintering temperature are 1-10 mbar, preferably 2-6 mbar and 0.5-3 mbar, preferably 1-2 mbar, respectively.

(2) Controlling the gas atmosphere during the increment from 1250-1350 °C up to the final sintering temperature is useful for eliminating the macroscopic Co gradient. However, the materials for which the currently invented process is useful suffer from enrichment of hard constituent containing W and Ta in a surface zone of ≤500 µm depth, accompanied by depletion of Co. The enrichment is such that in some cases the contents of

W and Ta in a range 0-10 μm from the surface are $\geq 20\%$ higher than that in the center of the body. It has surprisingly been found out that this enrichment can be eliminated by controlling the composition of the gas atmosphere during the plateau at the final sintering temperature. Both CO and N₂ must be controlled to achieve elimination of compositional gradients at a depth of $\leq 500\ \mu\text{m}$ from the surface of the body. The CO and N₂ partial pressures are 0.5-5 mbar, preferably 1-3 and 0.25-3 mbar, preferably 0.5-2 mbar, respectively during the plateau at the final sintering temperature.

(3) Controlling the gas atmosphere during temperature increment and the plateau at the final sintering temperature is not enough to obtain acceptable properties of the actual surface of the sintered body. It has been found out that by choosing proper CO and N₂ pressures when decreasing the temperature to a level well below the liquidus temperature of the binder phase, the surface composition at a depth of 0-10 μm is essentially the same as in the bulk. Surface layers of binder or hard constituents can thus be circumvented. The partial pressures of CO and N₂ are 0.25-3 mbar, preferably 0.5-2 mbar and 0.25-3 mbar, preferably 0.5-2 mbar, respectively during cooling from the final sintering temperature to $\leq 1200\ ^\circ\text{C}$.

Example 1

[0017] TNMG 160408-PF inserts were pressed using a powder mixture of nominal composition (at%) Ti 37.1, W 3.6, Ta 4.5, C 30.7, N 14.5 and Co 9.6. The green bodies were dewaxed in H₂ at a temperature below 350 $^\circ\text{C}$. The furnace was then evacuated and pumping was maintained throughout the temperature range 350-1300 $^\circ\text{C}$. From 350 to 1050 $^\circ\text{C}$, a temperature ramp of 10 $^\circ\text{C}/\text{min}$ was used. From 1050 to 1300 $^\circ\text{C}/\text{min}$, a temperature ramp of 2 $^\circ\text{C}/\text{min}$ was used. The temperature was held at 1300 $^\circ\text{C}$ in vacuum for 30 min. Subsequently, the vacuum valve was closed and the temperature was increased to 1480 $^\circ\text{C}$, using a ramp of 2 $^\circ\text{C}/\text{min}$. Up to 1310 $^\circ\text{C}$, the furnace pressure was allowed to increase due to outgassing of the porous bodies. During subsequent heating to the final sintering temperature, followed by cooling to 1200 $^\circ\text{C}$, gas mixtures were allowed to flow through the furnace while maintaining a constant pressure of 8 mbar. From 1310 to 1480 $^\circ\text{C}$ the gas mixture contained 8.3 vol% CO, 8.3 vol% N₂, the balance being argon (Ar). During liquid phase sintering for 90 min at 1480 $^\circ\text{C}$ the gas mixture contained 29.2 vol% CO, 12.5 vol% N₂, the balance being Ar. From 1480 to 1200 $^\circ\text{C}$ a cooling rate of 3.5 $^\circ\text{C}/\text{min}$ was applied, while using a gas mixture of composition 16.7 vol% CO, 12.5 vol% N₂, the balance being Ar.

[0018] Polished cross sections of the inserts were prepared by standard metallographic techniques and characterized using optical microscopy and electron microprobe analysis (EMPA). Optical microscopy showed that the inserts had an evenly distributed residual porosity in porosity class A04 or better throughout the sintered bodies. The pores were evenly distributed, without any pore concentration in the center of the body. Figure 1 shows an EMPA line scan analysis of Co, W, N and C ranging from one side of the insert, through the interior of the material to the opposite surface. Clearly the concentrations of all elements are constant throughout the insert, within reasonable measurement limits and statistical fluctuations.

Example 2 (comparative)

[0019] In a second experiment, inserts of nominal composition (at%) Ti 35.9, W 3.6, Ta 4.3, C 27.2, N 16.6 and Co 12.4 were manufactured in an identical manner as described in Example 1, except that the gas, that was allowed to flow through the furnace was Ar during the temperature increment from 1310 to 1480 $^\circ\text{C}$. In this case a typical macroscopic Co gradient was observed, having a parabolic shape, as can be seen in Figure 2, showing an EMPA line scan analysis. The Co content at a depth of 0-10 μm from the surface is 15 % lower than that in the center of the insert. Optical microscopy showed that the inserts had an evenly distributed residual porosity in porosity class A04 or better throughout the sintered bodies.

Example 3 (comparative)

[0020] In a third experiment, inserts of nominal composition (at%) Ti 37.1, W 3.6, Ta 4.5, C 30.7, N 14.5 and Co 9.6 were manufactured in an identical manner as described in Example 1, except that the gas mixture that was allowed to flow through the furnace was of composition CO 50 vol% and N₂ 50 vol% at a furnace pressure of 20 mbar during the temperature increment from 1310 to 1480 $^\circ\text{C}$. Optical microscopy of a cross section of an insert showed a concentration of pores in the center of the insert, porosity class worse than A08, whereas porosity was in porosity class A04 in a zone $\leq 500\ \mu\text{m}$ from the surface. EMPA line scan analysis indicated a minimum in Co content in the center of the insert. These two observations lead to the conclusion that the binder phase has melted from the outside and inward, trapping gas generated during temperature increment, resulting in unacceptable porosity and unwanted compositional gradients.

Example 4 (comparative)

[0021] In a fourth experiment, inserts of nominal composition (at%) Ti 37.1, W 3.6, Ta 4.52, C 30.7, N 14.5 and Co 9.6 were manufactured in an identical manner as described in Example 1, except that the gas mixture that was allowed to flow through the furnace was of varying composition during the temperature increment from 1310 to 1480 °C at varying furnace pressures. Moreover, the gas composition was different during liquid phase sintering and cooling to ≤1200 °C.

[0022] The table below, summarizes the gas composition in the furnace during sintering.

Temperature (°C)	Gas composition (vol%)			Furnace pressure (mbar)
	CO	N ₂	Ar	
1310-1340	50	50	0	1.5
1340-1370	55	45	0	3
1370-1400	67	33	0	4
1400-1430	75	25	0	5.5
1430-1480	75	25	0	6.5
1480 (plateau)	37	7	56	6
1480-1200	23	7	70	6

[0023] For comparison, inserts of another nominal composition (at%) Ti 40.2, W 3.6, C 27.2, N 16.6 and Co 12.4, i.e. without Ta, were manufactured in an identical manner.

[0024] Figure 3 and 4 show EMPA line scan analyses of the inserts made of the new alloy with Ta and the reference alloy without Ta, respectively. It is concluded from Figure 3 that no macroscopic Co gradient is observed of the type, shown in Figure 2. Hence, the gas atmosphere during the temperature increment from 1310 to 1480 °C is well balanced. However, there is a clear depletion of Co in a zone ≤500 µm from both surfaces. The Co content at a depth of 0-10 µm from the surface is 12 % lower than that in the center of the insert. This indicates an unbalance in the gas atmosphere during the plateau at the sintering temperature. The reference material shows essentially no compositional gradients. Optical microscopy showed residual porosity in porosity class A04 or better, throughout the insert for the Ta-containing material and no residual porosity, porosity class A00, for the reference material, without Ta.

Claims

1. Method of manufacturing by liquid phase sintering a body of titanium-based carbonitride alloy, containing hard constituents based on Ti, W and Ta in a Co binder phase, **characterized** in that the atomic N/(C+N) ratio is 25-50 at%, the Ta content is at least 2 at%, preferably 4-7 at%, the W content is at least 2 at%, preferably 3-8 at% and the Co content is 5-25 at% and that sintering is performed under such conditions that the liquid binder phase forms in the center of the body first and the melting front then propagates outwards towards the surface without generating a macroscopic binder phase gradient.
2. Method of manufacturing a sintered body according to claim 1, **characterized** in that sintering is performed under such conditions that essentially no depletion or enrichment of any of the constituents is observed in any part of the sintered body.
3. Method of manufacturing a sintered body according to any of the previous claims, **characterized** in that said body contains porosity in the class A06 or less, preferably A04 or less, evenly distributed throughout the volume, without a concentration of pores in the center of the body.
4. Method of manufacturing a sintered body according to any of the previous claims, **characterized** in that during temperature rise from a temperature 1250-1350 °C to the final sintering temperature, being 1370-1550 °C, the temperature increment rate is 0.5-5 °C/min.

EP 1 052 297 A1

5. Method of manufacturing a sintered body according to any of the previous claims, **characterized** in that during cooling between the sintering temperature and $\leq 1200^{\circ}\text{C}$ the temperature decline rate is $0.5\text{-}5^{\circ}\text{C}/\text{min}$.
- 5 6. Method of manufacturing a sintered body according to any of the previous claims, **characterized** in that during temperature rise from a temperature $1250\text{-}1350^{\circ}\text{C}$ to the final sintering temperature N_2 and CO partial pressures are kept constant or that N_2 and CO partial pressures are increased monotonously or stepwise.
- 10 7. Method of manufacturing a sintered body according to claim 6, **characterized** in that the N_2 and CO partial pressures are $0.25\text{-}3$ mbar, preferably $0.5\text{-}1.5$ mbar at 1300°C and that the N_2 and CO partial pressures are $0.5\text{-}3$ mbar, preferably $1\text{-}2$ mbar and $1\text{-}10$, preferably $2\text{-}6$ mbar respectively when reaching the final sintering temperature.
- 15 8. Method of manufacturing a sintered body according to claims 6 and 7, **characterized** in that the holding time at final sintering temperature is $30\text{-}120$ minutes.
9. Method of manufacturing a sintered body according to claims 6, 7 and 8, **characterized** in that the N_2 and CO partial pressures are $0.25\text{-}3$ mbar, preferably $0.5\text{-}2$ mbar and $0.5\text{-}5$ mbar, preferably $1\text{-}3$ mbar respectively during the hold at the final sintering temperature.
- 20 10. Method of manufacturing a sintered body according to claims 6, 7, 8 and 9, **characterized** in that the N_2 and CO partial pressures are $0.25\text{-}3$ mbar, preferably $0.5\text{-}2$ mbar and $0.25\text{-}3$ mbar, preferably $0.5\text{-}2$ mbar respectively during cooling from the final sintering temperature to $\leq 1200^{\circ}\text{C}$.
- 25
- 30
- 35
- 40
- 45
- 50
- 55

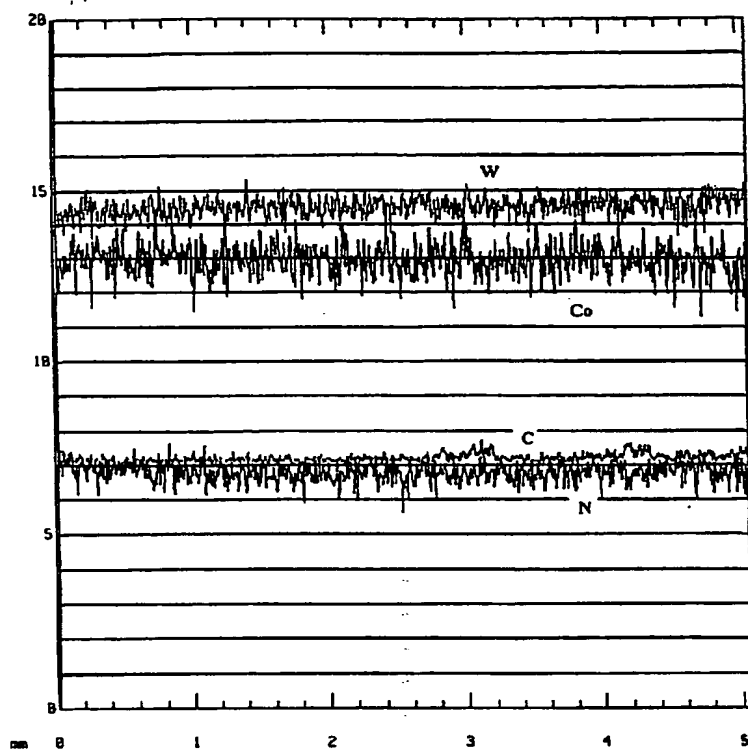


Fig. 1

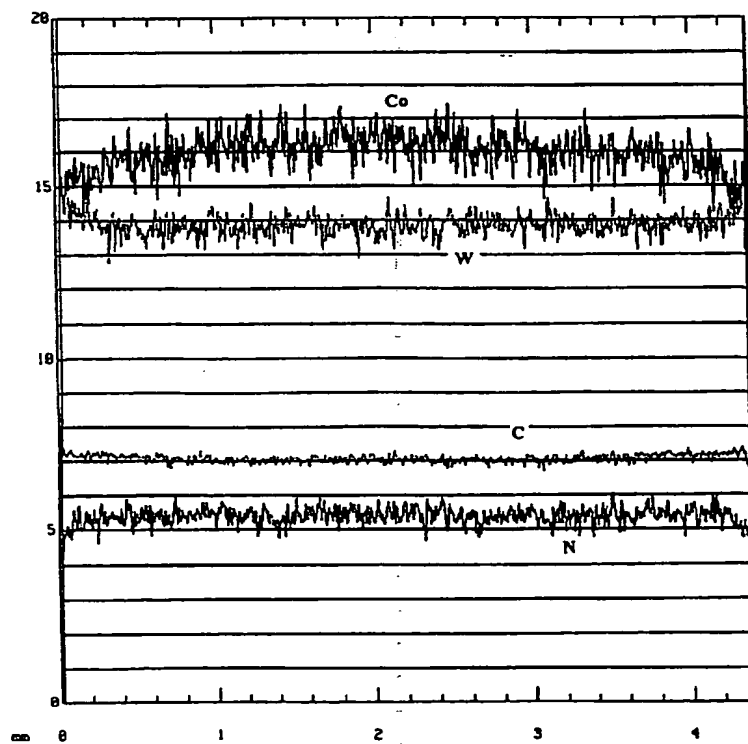


Fig. 2

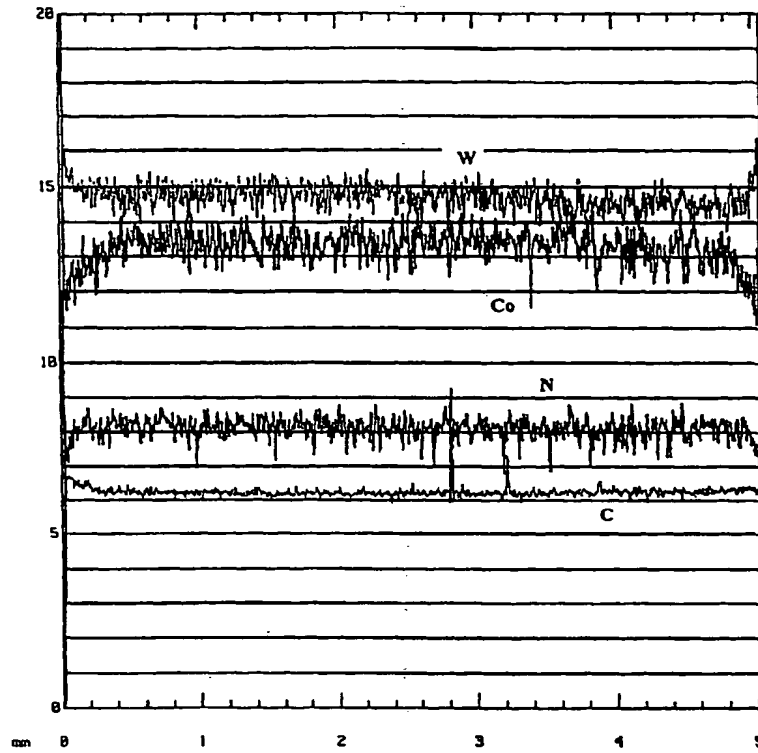


Fig. 3

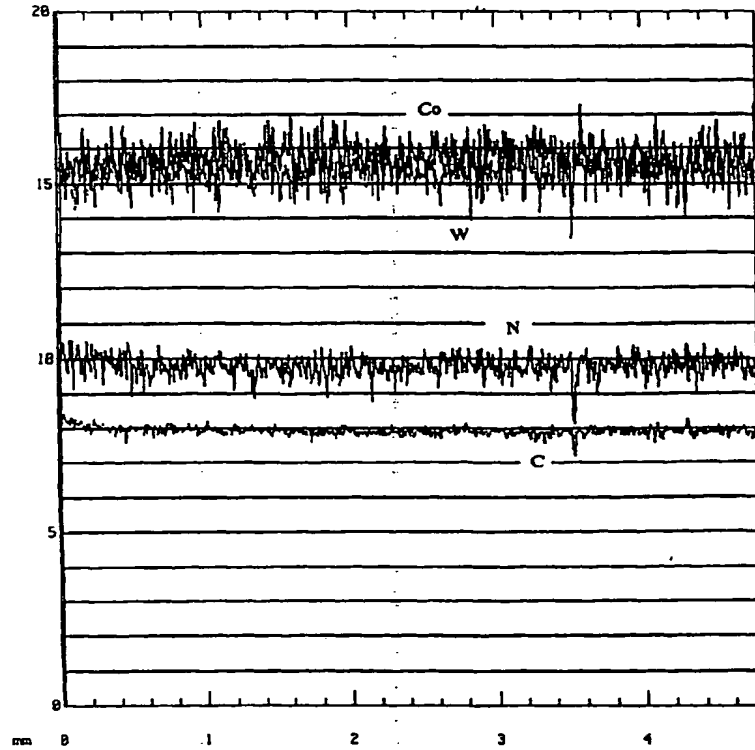


Fig. 4



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 10 9356

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 98 51830 A (SANDVIK AB PUBL) 19 November 1998 (1998-11-19) *page 3, lines 17 to 24, page 4, lines 17 to 21, page 5, lines 8 to 17, page 6, lines 18 to 29, page 8, lines 1 to 5 and Examples*	1-10	C22C1/05 C22C29/04
A	US 5 856 032 A (DREYER KLAUS ET AL) 5 January 1999 (1999-01-05) *column 3, lines 45 to 55, 66 to 67; column 5, lines 5 to 21 and Examples*	1-10	
A	EP 0 578 031 A (SANDVIK AB) 12 January 1994 (1994-01-12) * claim 4; example 1 *	1-10	
A	EP 0 519 895 A (SANDVIK AB) 23 December 1992 (1992-12-23) *page 2, lines 48 to 51; page 3, lines 14 to 21*	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C22C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 25 July 2000	Examiner Badcock, G
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (Pd/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 10 9356

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-07-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9851830 A	19-11-1998	SE 511846 C	06-12-1999
		EP 0996756 A	03-05-2000
		SE 9701858 A	15-01-1999
		US 5976213 A	02-11-1999
US 5856032 A	05-01-1999	DE 4423451 A	09-11-1995
		AT 163203 T	15-02-1998
		WO 9530030 A	09-11-1995
		DE 59501452 D	19-03-1998
		EP 0758407 A	19-02-1997
		ES 2112053 T	16-03-1998
		JP 9512308 T	09-12-1997
EP 0578031 A	12-01-1994	AT 141337 T	15-08-1996
		DE 69303998 D	19-09-1996
		DE 69303998 T	19-12-1996
		JP 6220559 A	09-08-1994
		US 5462574 A	31-10-1995
		US 5659872 A	19-08-1997
EP 0519895 A	23-12-1992	AT 135416 T	15-03-1996
		DE 69208947 D	18-04-1996
		DE 69208947 T	25-07-1996
		JP 5221725 A	31-08-1993
		US 5336292 A	09-08-1994